[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Infrared Spectra of *cis*- and *trans*-Propenyllithium. Stereochemistry of the Reaction of Vinyl Chlorides with Lithium Metal

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The *cis*- and *trans*-propenyl chlorides have been converted to propenyllithiums. An examination of the infrared spectra of the propenyllithiums permitted assignment of geometric structure to them, and showed that the chlorides were converted to lithium derivatives with retention of configuration.

Vinyl halides react to form vinyllithiums which in turn react with various reagents, such as carbon dioxide or benzaldehyde, to form the corresponding vinyl adducts. It is known that the geometrical isomer of the acid or alcohol obtained in these examples is such that the two reaction steps together have yielded over-all retention of configuration.[2] *A priori* this means that either both of the reaction steps have proceeded with retention of configuration, or else both have proceeded with inversion.[3] It is known that certain vinylic halides, for example bromobenzene, must undergo these reactions with retention in both steps, since if the first step went with inversion, phenyl-lithium would contain a *trans* double bond. From this evidence though, it can only be concluded that a vinyl halide can react to form a vinyllithium with retention. It does not prove that the reaction will proceed with retention when there is no geometrical constraint on the system.

This problem has been long recognized. Nesmeyanov and Borisov[4] have claimed that various halides, and in particular the 1-bromopropenes, have been shown to react to form the lithium derivatives with retention of configuration by what they call the "method of even and odd cycles." With regards to the application of the method to the present case, it can be seen that if formation and reaction of the propenyllithium always proceeds with the same stereochemistry, no matter what that stereochemistry is, the experimental results obtained necessarily follow. There is no way by the method of even and odd cycles to tell whether there have been two retentions or two inversions, except by analogy. Such an analogy can never be considered a proof. The only apparent way to determine the configuration of the vinyllithium intermediate is to examine the vinyllithium itself.

DISCUSSION

In the present work it was desired to prepare geometrically pure isomers of a vinyllithium, and to establish their structures by infrared spectra. The 1-propenyl system was chosen as most convenient. The *cis* and *trans* isomers of 1-chloropropene have had their structures established by dipole moment measurements.[5] The isomeric bromo compounds have been studied with regards to their stereochemical transformation by earlier workers, but they are not easy to work with as they equilibrate at a significant rate at room temperature.[6] The chloro compounds, which are stable to 135°, were therefore used.

It was established that under the conditions used in the present work the *cis*-1-chloropropene could be converted to a 1-propenyllithium, which in turn reacted with benzaldehyde to give the known[7] *cis*-1-phenyl-2-butene-1-ol, while the *trans* chloride led similarly to the *trans* alcohol.

The *cis*- and *trans*-propenyllithiums were prepared by the reaction of lithium metal and the chloride in ether solution. The solid propenyllithium was isolated under a nitrogen atmosphere, and a Nujol mull was prepared of it. The spectra of the two isomers were quite different, and the important features are recorded in Table I.

The out-of-plane hydrogen bending frequencies have been among the most useful for assignment of geometrical structure to olefins.[8] Almost all disubstituted olefins having a *trans* arrangement of hydrogens show this band at from 865 to 990

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[2] (a) E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951); (b) A. S. Dreiding and R. J. Pratt, *J. Am. Chem. Soc.*, **76**, 1902 (1954); (c) D. Y. Curtin and E. E. Harris, *J. Am. Chem. Soc.*, **73**, 2716 (1951); (d) D. Y. Curtin, H. W. Johnson, Jr., and E. G. Steiner, *J. Am. Chem. Soc.*, **77**, 4566 (1955).

[3] Various workers (a) D. Y. Curtin and W. J. Koeal, Jr., *Chem. & Ind.* (*London*), 262 (1960); (b) H. M. Walborsky and F. J. Impastato, *J. Am. Chem. Soc.*, **81**, 5835 (1959); (c) R. L. Letsinger, *J. Am. Chem. Soc.*, **72**, 4842 (1950); (d) D. E. Applequist, private communication, have recently shown that alkyl lithiums are formed and react with retention of configuration under certain circumstances.

[4] A. N. Nesmeyanov and A. E. Borisov, *Tetrahedron*, **1**, 158 (1957).

[5] N. B. Hannay and C. P. Smyth, *J. Am. Chem. Soc.*, **68**, 1005 (1946).

[6] K. E. Harwell and L. F. Hatch, *J. Am. Chem. Soc.*, **77**, 1682 (1955).

[7] D. Y. Curtin and J. W. Crump, *J. Am. Chem. Soc.*, **80**, 1922 (1958).

[8] For considerable discussion and a list of references, see L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, Wiley, New York, 1954, p. 31.

TABLE I

INFRARED SPECTRA OF 1-PROPENYLLITHIUMS PREPARED FROM THE CHLORIDES OF INDICATED CONFIGURATION[a]

cis	*trans*
2760 (W)	2725 (W)
2050 (W)	2070 (W)
1540 (S)	1555 (S)
1127 (W)	1230 (M)
1035 (S)	1045 (S)
	1030 (M)

[a] Most of the C—H bending and stretching frequencies are obscured by the Nujol, and they are not indicated.

cm.$^{-1}$ The presence of a highly electronegative atom on the double bond, such as in *trans*-propenyl chloride, lowers this frequency by some 30 cm.$^{-1}$, and it is expected that the electropositive lithium should increase the frequency by a similar amount.[9] In the present case neither isomer shows absorption in the range 965–990 cm.$^{-1}$ The strong absorption near 1040 cm.$^{-1}$ of each isomer is probably due to the C—Li stretching vibration.[10] This leaves the medium band at 1030 cm.$^{-1}$ in the isomer obtained from the *trans* chloride as the best candidate for the *trans*-out-of-plane bending frequency.[11] The other isomer shows only the C—Li band in this region. On this basis the *trans* structure can be assigned to the lithium derivative obtained from the *trans* halide.

It seems to be rather generally true that the C=C stretching frequency is higher for a *trans* disubstituted ethylene than it is for its *cis* isomer, regardless of whether the attached groups are electropositive or electronegative. For example, simple alkenes show this band at 1673 and 1657 cm.$^{-1}$ for *trans* and *cis* isomers respectively.[8] The propenyl chlorides absorb at 1681, 1648 (doublet), and 1639, 1605 (doublet) cm.$^{-1}$, respectively, while for the bromomercury propenes the frequencies are 1625 cm.$^{-1}$ and 1510, 1600 cm.$^{-1}$ (doublet). The *trans*- and *cis*-propenyllithiums (as assigned from the out-of-plane bending frequencies) have C = C stretching frequencies at 1555 and 1540 cm.$^{-1}$ respectively, and this is consistent with the assignment made.

The infrared spectra of *cis*- and *trans*-propenyllithium have also been reported by Nesmeyanov, Borisov and Novikova.[4,12] Their spectra bear little resemblance to those obtained in the present work. In particular they report absorption for the *trans* and *cis* isomers respectively at 1645 and 1623 cm.$^{-1}$ for the C = C stretching modes (under unspecified conditions) and at 975 and 700 cm.$^{-1}$ for the out-of-plane bending. These values are similar to those of the starting materials and propenyl derivatives such as might be obtained from various side reactions.

According to Walsh,[13] the C = C stretching frequency is increased by the joining of an electronegative atom to one of the carbons. The electronegative atom tends to pull electrons out toward it, and since p electrons are further from the carbon than s electrons, the result is to increase the p character of the bond toward the electronegative atom. The p character of the σ component of the C = C bond is consequently decreased, which increases the C = C bond strength and raises the frequency. It can therefore be concluded that the reverse should occur when an electropositive atom is attached to carbon. According to this view, a decrease in this frequency is expected when an electropositive atom replaces a hydrogen atom on the double bond. The low C = C frequencies observed for the propenyllithiums are qualitatively as expected, and it is difficult to imagine to what other kind of structure they could be assigned. Samples of the solid alkenyl lithiums which were isolated were seen to blacken, smoke, generate considerable heat, and sometimes ignite when exposed to air, and there seems to be no question but that the spectral bands listed in Table I actually are of the propenyllithiums. It is not clear to what compounds the spectra reported by Nesmeyanov and coworkers[12] are to be attributed.

On the basis of the infrared spectra of the propenyllithiums it can be concluded that they are formed and react exclusively with retention of configuration under the conditions used. It therefore seems likely that in the general case vinyllithiums are formed and react preferentially with retention of configuration.

EXPERIMENTAL[14]

cis and *trans*-Propenyl chloride. One liter of commercial 1,2-dichloropropane was purified by washing it with concentrated sulfuric acid, followed by distillation. This material was then added dropwise to a refluxing solution of alcoholic potassium hydroxide. Material boiling below 60° was continuously removed by distillation. The distillate was washed with water, dried over calcium chloride, and then fractionally distilled through a 4-foot helix-packed column. The low and high boiling fractions were separately refractionated and gave respectively the *cis* isomer, b.p. 30.8–31.3°, and *trans* isomer, b.p. 37.9°. The infrared spectra indicated that neither isomer contained more than 2% of the other. About 100 g. of each was obtained. The isomers

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[9] (a) N. Sheppard and G. B. B. M. Sutherland, *Proc. Roy. Soc.*, **196A**, 195 (1949); (b) R. E. Kitson, *Anal. Chem.*, **25**, 1470 (1953); (c) W. J. Potts and R. A. Nyquist, *Spectrochim. Auta*, **14**, 679 (1959).

[10] (a) T. L. Brown and M. T. Rogers, *J. Am. Chem. Soc.*, **79**, 1859 (1957); (b) A. N. Rodionov, D. N. Shigorin, T. W. Talalaeva, and K. A. Kocheshkov, *Doklady Akad. Nauk. (SSSR)*, **123**, 113 (1958).

[11] The bands at 1030 and 1045 cm.$^{-1}$ are given the indicated assignments on the basis of their relative intensities. These two assignments could be reversed without affecting the present conclusions.

[12] A. N. Nesmayanov, A. E. Borisov, and N. V. Novikova, *Doklady Akad. Nauk.*, **119**, 504 (1958).

[13] A. D. Walsh, *Disc. Faraday Soc.*, **2**, 18 (1947).

[14] The authors are indebted to Miss B. Bach for determining the infrared spectra described.

were identified by boiling point,[15] and by the presence of an intense hydrogen out-of-plane bending band at 924 cm.$^{-1}$ in the infrared spectrum of the *trans* compound.

cis and *trans*-Propenyllithium. This procedure is representative. A solution of 4 g. of *cis*-propenyl chloride in 15 ml. of ether was stirred vigorously under nitrogen with a two-fold excess of lithium metal[16] for 3 hr.

The reaction mixture was then filtered (in a dry box under nitrogen) to remove lithium metal and some salts. The filtrate was then evaporated under vacuum, and the residue was used to prepare a mull in Nujol. This mull was placed in an infrared cell, which could then be handled in air.

A modification of this procedure eliminated the filtration above. The pieces of lithium metal were picked out by hand, and after evaporation of the volatile material, the remainder of the solid was used for the mull. The principal bands obtained and assigned to the propenyllithium were the same in either method. Some small variable bands were also obtained, and since they were not consistently present in samples prepared in different runs, they were clearly due to impurities and were not further considered. The infrared spectra were recorded on both a Beckman IR-4 and a Baird Spectrophotometer.

trans- and *cis*-1-Phenyl-2-butenol-1. The reaction mixture containing propenyllithium from the *trans* chloride was cooled to 5° and 2 g. of benzaldehyde was added dropwise with stirring. After stirring the mixture an additional 20 min. at 5° the solution was filtered to remove excess lithium, and a cold saturated solution of ammonium chloride was added to the filtrate. The phases were separated, and the aqueous phase was extracted with ether. The combined ether layers were dried over potassium carbonate, and the ether was evaporated. Distillation furnished 2 g. of material, b.p. 103–110° (0.25 mm.). The infrared spectrum showed a strong band at 965 cm.$^{-1}$ which is characteristic of the *trans* isomer, and it was not detectably contaminated by the *cis*, which absorbs at 980 cm.$^{-1}$

The *cis* chloride similarly yielded the *cis* alcohol, which showed strong absorption at 980 cm.$^{-1}$, and was not detectably contaminated with the *trans*.

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(15) E. H. Huntress, *Organic Chlorine Compounds*, Wiley, New York, 1948, p. 947.

(16) It was found that lithium from some batches consistently reacted very well, while that from other batches consistently failed to react. J. A. Beel, W. G. Koch, G. E. Tomasi, D. E. Hermansen, and P. Fleetwood, *J. Org. Chem.*, 24, 2036 (1959) have shown that the sodium content of the lithium can greatly affect its reactivity toward halides. The quality of the lithium used in the present work is not known.

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1,6-Reductive Coupling of Hindered *o*-Vinyl Diaryl Ketones[1]

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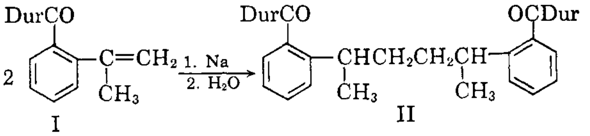
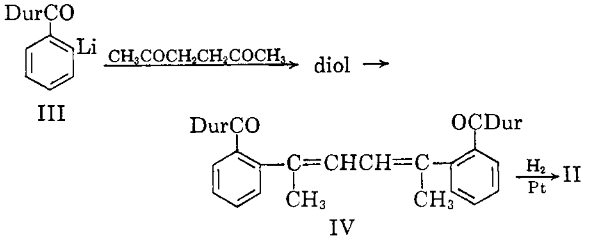
Mesityl *o*-vinylphenyl ketone, duryl *o*-vinylphenyl ketone, and duryl *o*-isopropenylphenyl ketone have been reduced with metallic sodium, the products being the corresponding butanes to be expected from 1,6-reductive coupling involving the side chain. The reductive coupling product of the isopropenyl compound was isolated in the expected two diastereoisomeric forms. These compounds were synthesized independently from *o*-duroylphenyllithium and acetonylacetone. The diol was dehydrated, and the resulting diene was hydrogenated catalytically.

1,6-Addition of Grignard reagents to hindered ketones is well known, and in the reaction of *t*-butylmagnesium chloride with duryl *o*-isopropenylphenyl ketone was shown to involve the *p*-position rather than the side chain.[4] The formation of *p,p'*-diduroylbiphenyl from duryl *p*-hydroxyphenyl ketone[5] depends on a 1,6-coupling. It has now been found that a similar coupling involving the side chain can be realized by treating hindered *o*-vinylphenyl ketones with sodium. The hexane derivatives II produced in this way from duryl *o*-isopropenylphenyl ketone (I) correspond to the two diastereoisomeric forms to be expected.



Their structure was established by an independent synthesis beginning with the condensation of *o*-duroylphenyllithium (III)[6] with acetonylacetone. The crude diol was dehydrated with dilute sulfuric acid to give 1,4-di (*o*-duroylphenyl)-1,4-dimethylbutadiene (IV). Hydrogenation of the diene produced a mixture of the two diastereoisomeric hexane derivatives. When isolated in pure form they were found, by reference to mixture melting point deter-



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[2] Socony-Vacuum Oil Company Fellow, 1954–55.

[3] Deputationist of the Government of the Union of Burma.

[4] R. C. Fuson, W. D. Emmons, and S. G. Smith, Jr., *J. Am. Chem. Soc.*, 77, 2503 (1955).

[5] R. C. Fuson and G. W. Parshall, *J. Am. Chem. Soc.*, 76, 5561 (1954).

[6] R. C. Fuson, W. C. Hammann, and W. E. Smith, *J. Org. Chem.*, 19, 674 (1954).